

Willmar, Minnesota Controls Nitrification in Distribution System

Part 1: Ozonation

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Summary

Previous studies, reported in Public Works (October-December, 1997), showed that chloramine was the principal cause of elevated copper levels in water withdrawn from household plumbing after 6 hours of retention. In an effort to reduce chloramine concentrations throughout the Willmar water distribution system, the present studies were undertaken to find a practical means for removing ammonium ion from the Willmar groundwater supply. Ammonium ion removal was expected to reduce microbially-mediated nitrification, thereby reducing the formation of nitrite and nitrate ion during distribution. In the absence of reducing agents, it was believed that chloramine residuals would be stabilized so that lower residual concentrations could be applied to the finished water leaving the treatment plant.

Introduction

Studies conducted at Willmar, MN in July and August, 1996, provided strong evidence that *chloramine* was the strongest factor influencing the short-term rate of corrosion of copper pipe. The results of these studies indicated that decreasing finished water chloramine to levels approaching 1 mg Cl/I should limit copper corrosion in household plumbing to less than the 1.3 mg Cu/I copper action level.

The barrier to decreasing the level of chloramine leaving the treatment plant was the loss (consumption) of disinfectant during distribution. In the absence of microbial activity or reaction with the surface of distribution piping, low levels of chloramine can persist for hundreds of hours in finished water. However, when sufficient ammonium ion is present, nitrifying organisms will proliferate and oxidize the ammonium ion to nitrite and, ultimately, nitrate ion.

Nitrite ion, in particular, is a strong reducing agent. It combines rapidly with the chloramines to consume the residual in hours instead of days. This was the existing situation in the Willmar distribution system. High concentrations of ammonium ion in the well waters had resulted in the colonization of the distribution system with nitrifying bacteria which mediated the conversion of ammonium to nitrite ion.

In addition to the discoloration of poultry products, the presence of nitrite ion in the water distribution system could constitute a health concern (methemoglobinemia). Nitrite is therefore regulated at 1 mg N/I. For this reason alone, the control of the activity of nitrifying organisms is indicated.

The basic control strategy can therefore be summarized, as follows:

- Reduce chloramine applied as a distribution system residual.
- Control the loss of chloramine in distribution system.
- Control formation of nitrite during distribution.
- Control nitrifying bacteria in the distribution system.

Oxidation of Ammonium Ion by Ozone

The literature on ozonation indicates that it is possible to *directly* oxidize ammonium ion using *ozone*. The reported reaction is comparatively slow (requires hours of contact in the absence of catalytic agents), is temperature-dependent and is accelerated at higher pH.

The application of ozone to ground water is expected to result in the rapid oxidation of reduced *iron*, *manganese*, *sulfides* and a portion of the *organic carbon* present. The oxidation of the naturally-occurring organic compounds (humic and fulvic acids) is known to reduce color and diminish the formation of disinfection by-products, such as the trihalomethanes.

Ozonation is also believed to completely *sterilize* the treated water. Since ozone will independently oxidize the manganous ion present, the present permanganate feed could be discontinued. However, post-chlorination would still be required to provide a stable distribution system disinfectant residual since ozone will not persist.

It is known that most waters will not sustain a residual ozone concentration in aqueous solution for long periods. However, higher alkalinity waters allow ozone to persist for longer periods (hours), enhancing direct reactions with aqueous (dissolved) ozone.

Of the options available, ozonation appeared to offer the promise of combined oxidation and disinfection. A critical need was to determine under what operational conditions the application of ozone to Willmar water might result in ammonium ion oxidation.

It was hypothesized that, if ammonium ion concentrations could be reduced by half and if distribution system chloramine residuals could be maintained at 1 mg Cl/l or less, copper corrosion rates might be reduced to below the copper action level as evidenced by the previous copper pipe test loop studies.

Ozonation Pilot Plant Study Results

The principal objective of the proposed study plan was to evaluate the effectiveness of ozonation as a unit process to augment the treatment presently provided by Willmar.

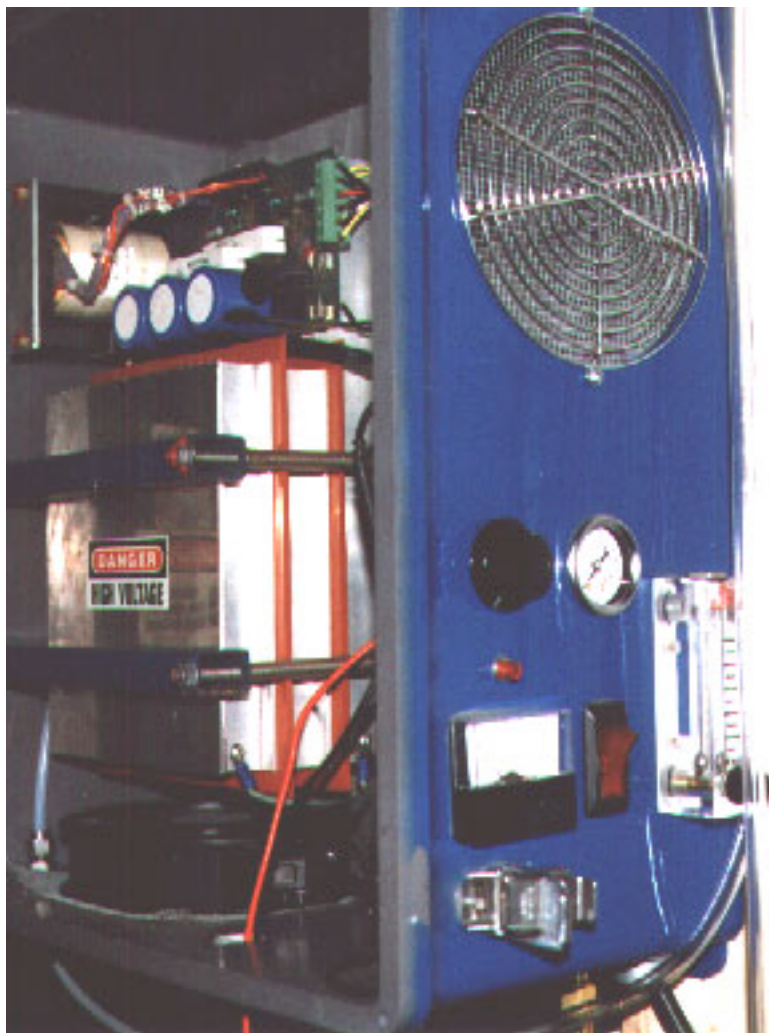
To perform the tests, a 10 gpm ozonation pilot plant unit was installed at the Southwest treatment plant. The pilot plant utilized a compressed oxygen feed to a corona-discharge ozone generator. The ozonated oxygen was then applied to the aerated plant water through an ozone injector, contactor and degasifier. Following the absorption of ozone, a greensand filter was used to determine the filterability of the ozone-oxidized byproducts.

The comparative effect of ozone on filtered water quality was then evaluated with respect to:

- iron and manganese oxidation and filtration
 - sulfide oxidation
 - total organic carbon and color reductions
 - ammonium ion oxidation
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- The study results indicated that ferrous iron had already been effectively oxidized by oxygen in the aerated water.
 - Manganous (II) ion was first oxidized by ozone to permanganate (VII), giving the ozonated water the characteristic clear, pink color of permanganate. On filtration through greensand, this permanganate was chemically reduced and the resulting manganese dioxide precipitate effectively removed.
 - Sulfides, which were low in the influent water, were undetectable in the ozonated water.
 - While organic color was significantly reduced, there was only a 20% reduction in total organic carbon.
 - However, little oxidation of ammonium ion was achieved even at pH values up to 9.0. As a result, the ozonation

studies were eventually discontinued for lack of effectiveness.

- **Ozonation for Oxidation of Ammonium Ion**



Ozone Generator

A small, wall-mounted ozone generator (Sun River Innovations, Limited: Trilogy, Model G22) was selected for the pilot plant studies. Dry, compressed oxygen (100% O₂, 2000 psig, 200 scf/tank) rather than air (21% O₂) was used as the feed gas to the ozone generator to allow for higher ozone outputs. A small rotameter (seen at the right of the ozonator box) provided final regulation of the influent oxygen flow rate up to 20 standard cubic feet per hour (scfh) at 6 psig pressure. The gas then passed through charged, dielectric-coated parallel flat plates (left, center) where several percent of the oxygen applied was converted to ozone in a corona discharge.

Power for the generator was provided by a 3-wire, 115 Volt, 50/60 Hertz, 15 Ampere service. A potentiometer (0 - 5 V DC) varied power input while a red indicator light indicated the generator operation. The unit was air-cooled by a small fan (Note grill located on the right hand side of the box.). Temperature control is critical because the corona discharge creates heat. High plate temperatures markedly reduce ozone generator output efficiency leading to large variations in ozone production and absorption.



Ozonation System: Flat-Plate Ozone Generator, Venturi Injector (Mazzei),
Contacting Tank (WMU, blue column) and Degassing Separator (GDT, stainless steel)

Description of Ozonation System

The ozonated oxygen was aspirated through a Venturi tube (Mazzei Injector Company) into a 1 gallon contactor (GDT Corporation, Phoenix, AZ) which provided 10 seconds of contact between the ozonated gas and the aerated Southwest plant water. The specified ratio of gas to liquid volume was approximately 0.1 at a outlet back pressure of 25 to 34 psig.

Subsequently, when experimental results indicated that the ozone absorption contactor did not provide sufficient retention time for oxidation of ammonium ion, the Willmar Municipal Utility Water Department staff fabricated a larger, (blue plastic) contactor tank to increase the contact detention time to 120 seconds.

Following gas/liquid contact for the absorption of ozone, the remaining gas (primarily, oxygen, since the influent water was initially saturated with oxygen) must be separated. The cylindrical stainless steel column is the degassing separator.

The off-gas from the separator, because it still contains the ozone gas which has not been absorbed, was passed through an ozone 'destruct' unit. This consisted of an 18-inch long, 4-inch diameter PVC column filled with granular activated carbon. Granular activated carbon, a reducing agent, reacts readily with ozone to produce heat and carbon dioxide. Since heat build-up creates danger from fire, the off-gas was subsequently routed into the Southwest plant aeration tower.

The ozonated water was then pumped to a pair of 7-foot high, 3-foot diameter steel tanks in series. The first tank contained a 3-foot depth of greensand filter medium, 0.3 to 0.35 mm in effective diameter. The second tank remained empty pending a decision as to adding granular activated carbon as a post-adsorber for the partially-oxidized, biologically-degradable organic by-products produced by ozonation.

Finally, a polyethylene tank was provided as a clear well and to provide contact time for post-chlorination.



Oxygen Cylinder and Ozonator Generator, Pump, Injector and Contactor (lower left, black), SS Degassing Separator , Ozone Destruct Column (black), Filter Columns in Series (center), Clear Well (right)

Ozonation Study Results: Ozone Persistence and Color Reduction

Operation of the ozone system indicated that, while the ozonator output and absorption of ozone was inconsistent, the ozone concentrations produced in the aerated water influent were persistent.

Data from the initial test, shown on Figure 1, indicates that some ozone persisted for more than three hours. Despite this, ammonium ion was not significantly oxidized under these test conditions (pH 8).

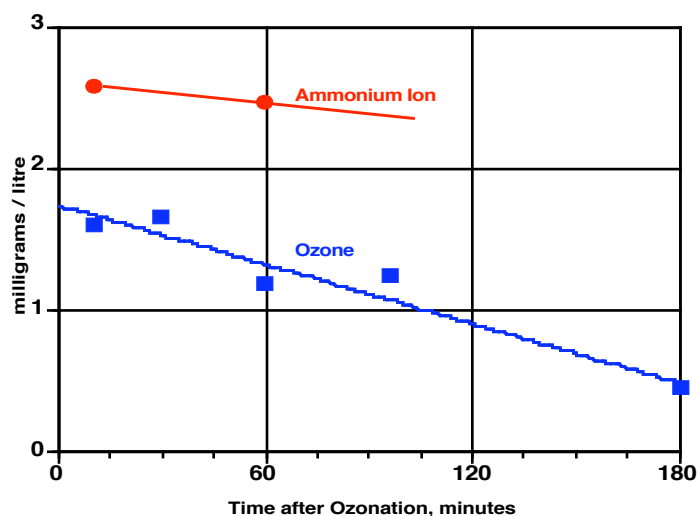


Figure 1. Ozone and Ammonium Ion Persistence

A more controlled study was conducted using Southwest plant water under the following initial conditions: Temperature, 10 °C; pH, 8.05; Color (true), 14 color units; NH_4^+ , 2.52 mg N/l. After aeration, color (apparent) had increased to 44 units due to the precipitation of orange-brown iron oxides. Subsequently, greensand filtration removed the ferric oxide solids so that the residual true color was again 14 color units.

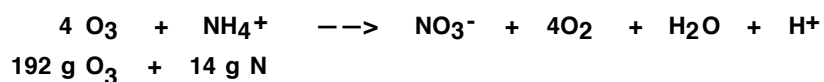
The application of ozone oxidized the manganous ion in the source water to the pink permanganate ion. After passage of this ozonated water through the greensand filter, the permanganate was reduced, the precipitate removed and the true color reduced to 5 color units. The overall color reduction may have resulted from the conversion of the organic matter initially present in the Southwest water to a more oxidized organic form.



Color: (aerated) (aerated, filtered) (ozonated, filtered) (ozonated)

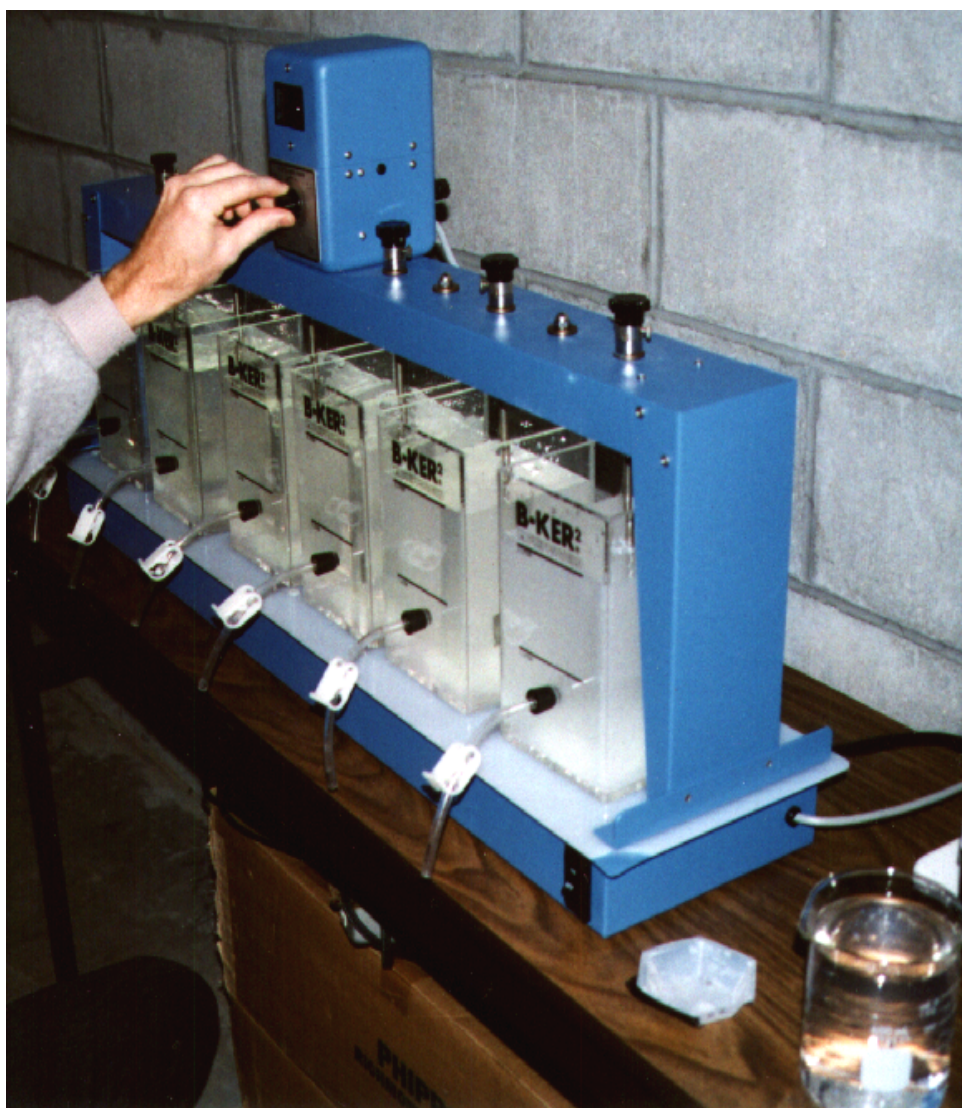
Ozone Oxidation of Ammonium Ion: pH Adjustment with MgO

At high pH and in the presence of a persistent ozone residual, ozone has been shown to be capable of oxidizing ammonium to nitrate ion according to the following relationship:



Since approximately 13.7 mg of ozone would be required to oxidize 1 mg of ammonium ion as nitrogen, high ozone dosages are required.

Early tests indicated that ozone persisted for hours in Willmar well water, possibly owing to its high alkalinity. However, in an effort to introduce pin-point regions of high pH in the Southwest plant water, magnesium oxide (MgO) powder was applied in a variety of dosages ranging from 0 to 500 mg/l.

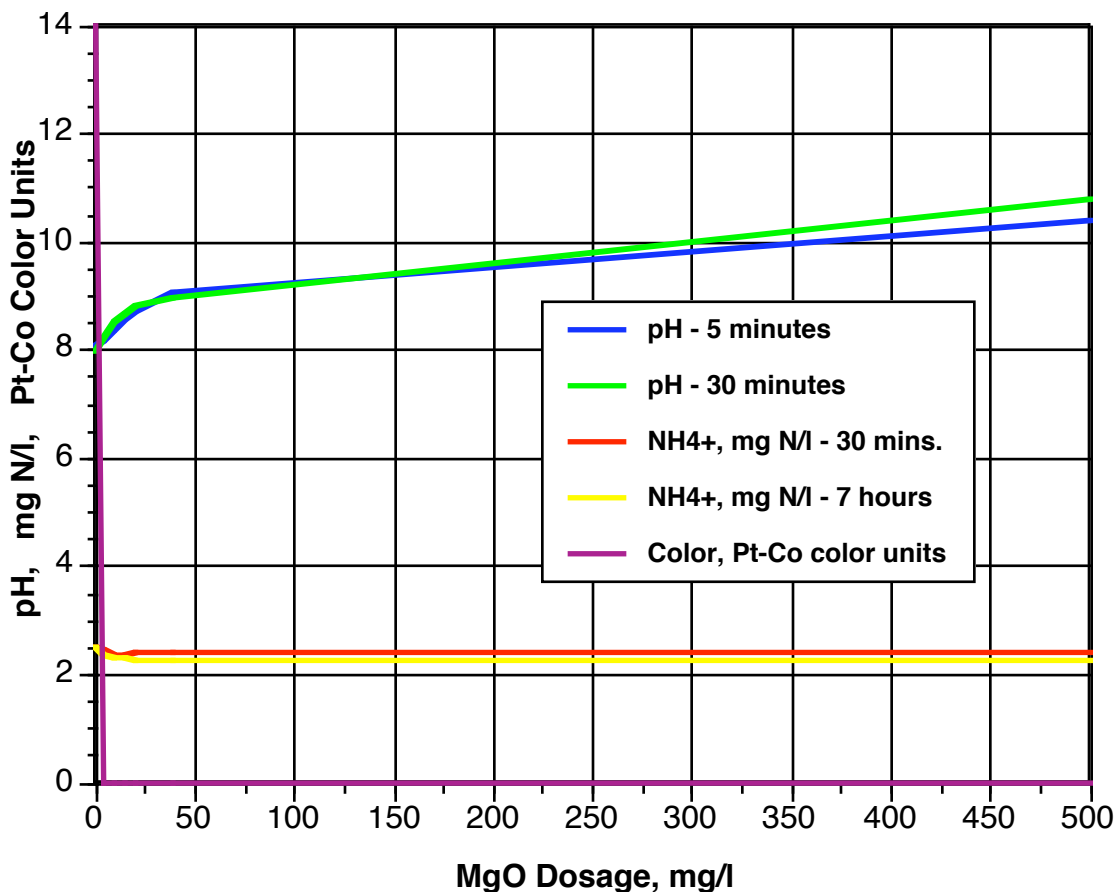


Addition of MgO to Ozonated Southwest Plant Water for Ammonium Ion Oxidation

After the addition of MgO to jar test beakers, the samples were rapid mixed for two minutes and , then, slow mixed at

100 rpm for 30 minutes. Samples were taken for analysis for pH and ammonium ion 5 and 30 minutes after the start of the slow mix. The results, presented in Figure 2, show that a barely measurable reduction in ammonium ion had been achieved. The initial ozone concentration was approximately 5 mg/l.

Figure 2. Ozone Oxidation of Ammonium Ion with Addition of MgO to increase pH



Pilot plant studies conducted under continuous flow conditions (10 gpm) indicated that the Willmar well water exerted little ozone demand. While, following ozone absorption, the water contained between 4 and 5 mg O₃/l, an ozone residual of 3 mg O₃/l remained after 10 minutes. This residual was accompanied by the pink permanganate ion produced by the ozonation of the manganous ion in the well water.

Following greensand filtration, the permanganate ion had been completely reduced and removed. In addition, the yellow-brown dissolved organic matter had been oxidized to colorless, but potentially degradable, organic compounds by ozonation. Finally, greensand filtration had removed all traces of the ozone.

The pilot plant studies also indicated that virgin greensand alone was capable of removing about 10% of the ammonium ion applied. Subsequent controlled column studies showed that the greensand adsorbed or exchanged 0.1 mg of ammonia N per gram of greensand.

Before additional 'ozonation plus MgO treatment' studies could be conducted under different conditions, an electrical breakdown in the ozone generator terminated pilot plant operation and caused a change in the study program.

Part 2 of this report will detail the development of the breakpoint ammonia reduction treatment (BART) protocol and its successful application to the Willmar treatment plants. In addition, data from a year-long monitoring survey of the distribution system remediation will be presented. These data confirmed the effectiveness of the BART protocol in controlling nitrification in the distribution system.